

REACTIONS ORIGINATING FROM UPPER EXCITED SINGLET STATES S_n ($n \geq 3$): THE PHOTOCHEMICAL CYCLOREVERSION OF SEVERAL ENDOPEROXIDES OF THE TETRACENE SERIES

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Summary

The photochemical cycloreversion of four endoperoxides of the tetracene series was investigated in the wavelength region from 313 to 248 nm. A strong wavelength dependence of the corresponding quantum yield Q_1 was observed throughout this spectral region.

A comparison of the electronic spectra of the unsymmetrical endoperoxides with the spectra of their individual chromophores indicates that the singlet manifold of the endoperoxides is composed additively of the excited singlet states of three different chromophores. Obviously the distinct wavelength dependence of Q_1 reflects the high density of excited singlet states S_n ($n \geq 3$), from each of which the reaction channel of cycloreversion is accessible. In contrast, the S_1 state and, surprisingly, also the S_2 state are photochemically inactive with respect to the cleavage of the endoperoxides into hydrocarbon and oxygen. Possible reasons for the inactivity of the S_2 state are discussed.

1. Introduction

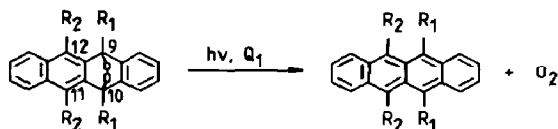
Relatively few photochemical reactions in the condensed phase have been reported in the past to occur from upper excited electronic states S_n or T_n ($n \geq 2$) [1]. As the actual chemical reaction step has to compete with the normally very rapid internal conversion (IC) to S_1 or T_1 , only a small number of simple and extraordinarily fast monomolecular reactions may be considered to be possible candidates for this type of photochemical reaction. Most of these are bond isomerizations, during which the total number of rings per molecule is altered, *e.g.* the photoisomerization of Dewar naphthalene [2] and the photochemical rearrangement of polycyclic cyclobutenes [3]. Also a few concerted bond cleavages belong to this group, *e.g.* the photodissociation of the anthracene-tetracene dimer [4].

Recently, we found that the cycloreversion of various endoperoxides of the anthracene series and of several structurally related photochromic endoperoxides, regenerating the parent hydrocarbon and oxygen, also originates from upper excited electronic states [5 - 8]. Obviously the release of oxygen from these endoperoxides also belongs to the class of particularly fast photochemical processes. In accordance with this conclusion Eisenthal and coworkers [9] reported an upper limit for the cycloreversion reaction time of 5 ps for irradiation at $\lambda = 266$ nm.

The absence of inner and outer heavy-atom effects on the photochemical cleavage of heterococordianthrone endoperoxide [10] indicates that the cycloreversion of endoperoxides originates from an upper excited singlet state S_n ($n \geq 2$). This result confirms the theoretical considerations of Kearns and Khan [11].

For the majority of the endoperoxides investigated so far the cycloreversion channel is reached on excitation to the S_2 state. 1,4,9,10-tetraphenylanthracene endoperoxide (TPAPO), however, shows a characteristic gradual wavelength dependence of the quantum yield from which we conclude that for this compound cycloreversion may be initiated not only from the thermalized S_2 state but also directly from the S_3 state [6].

The question of whether this is a unique case can only be resolved on the basis of further systematic studies. We therefore extended our investigations on endoperoxides of the tetracene series:



We studied tetracene endoperoxide (TPO; $R_1 \equiv R_2 \equiv H$), 9,10-diphenyltetracene endoperoxide (DPTP01; $R_1 \equiv C_6H_5$, $R_2 \equiv H$) and rubrene endoperoxide (RUBPO; $R_1 \equiv R_2 \equiv C_6H_5$), where in each case the O—O bridge connects positions 9 and 10, and 9,10-diphenyltetracene endoperoxide (DPTP02; $R_1 \equiv C_6H_5$, $R_2 \equiv H$) where the O—O bridge is attached to carbons C(11) and C(12).

During the photolysis of these endoperoxides cycloreversion competes with irreversible photochemical rearrangement reactions. In the present paper, however, we restrict ourselves to the discussion of the wavelength dependence of the cycloreversion quantum yield Q_1 .

2. Experimental details

Tetracene was purchased from EGA and recrystallized from toluene. 9,10-diphenyltetracene and rubrene were prepared following known procedures [12, 13]. The synthesis of the endoperoxides was accomplished in CS_2 by self-sensitized photo-oxidation applying sunlight. Immediately after

decolourization the light was shut off and the solutions were further treated in the usual way [5]. After purification by column chromatography (silica gel; benzene:CHCl₃, 3:2) colourless crystals of TPO and RUBPO were obtained. The colourless oxidation product of 9,10-diphenyltetracene, obtained in the same way, was a mixture of DPTP01 and DPTP02. However, by subsequent column chromatography (silica gel; toluene:heptane, 3:1) complete separation of these endoperoxides was achieved (DPTP01 was the first fraction to leave the column). CH₂Cl₂ and heptane (Merck; spectroscopic grade) were used as solvents for the quantitative experiments.

The electronic spectra were recorded on a Perkin-Elmer 555 spectrophotometer. All irradiations were performed with nitrogen-purged solutions at 22 ± 3 °C on an apparatus described previously [14]. Absolute monochromatic quantum fluxes were determined using a calibrated photodiode and a reusable chemical UV actinometer, Actinochrome R (248/334), recently developed by us and now commercially available from Amko, Tornesch [15].

Q_1 was determined by monitoring the formation of the parent hydrocarbons spectrophotometrically at the first absorption maximum. The evaluation method employed has been described in detail in ref. 5.

3. Results and discussion

3.1. Energy levels of the singlet states

The electronic spectra of TPO, DPTP01, DPTP02 and RUBPO are given in Figs. 1 - 4. On a phenomenological basis they can be divided into two groups. The spectra of TPO and DPTP01 are almost identical as can be seen from Figs. 1 and 2. The remaining spectra of RUBPO and DPTP02 also

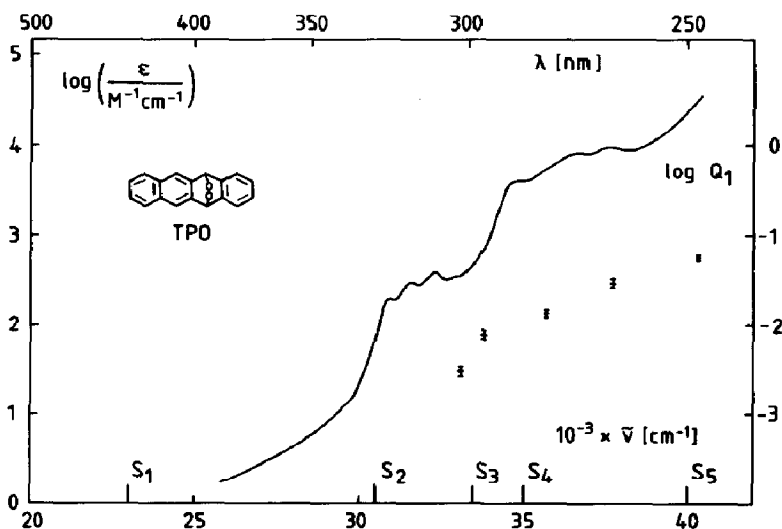


Fig. 1. Electronic spectrum of TPO (solvent, CH₂Cl₂): $\bar{\epsilon}$, values for the quantum yield Q_1 with error limits; $S_1 - S_5$, energy locations of excited singlet states.

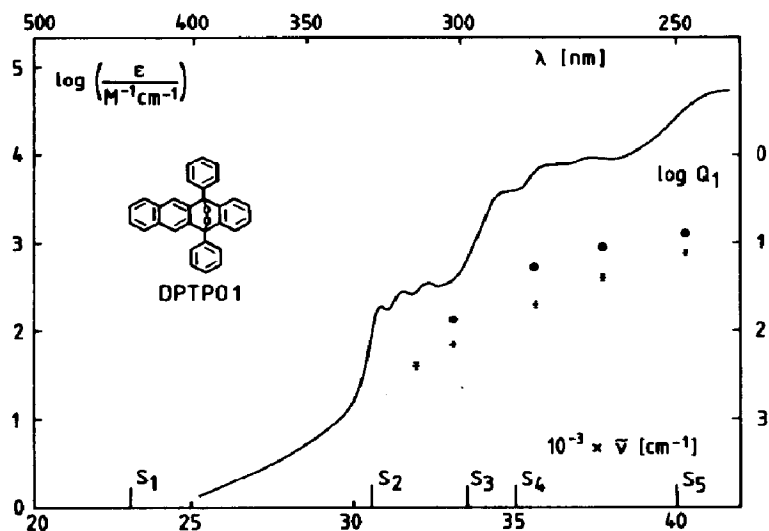


Fig. 2. Electronic spectrum of DPTP01 (solvent, CH_2Cl_2): $\bar{\epsilon}$, values for the quantum yield Q_1 with error limits; $S_1 - S_5$, energy locations of excited singlet states; \bullet , values for the quantum yield Q_1 in heptane.

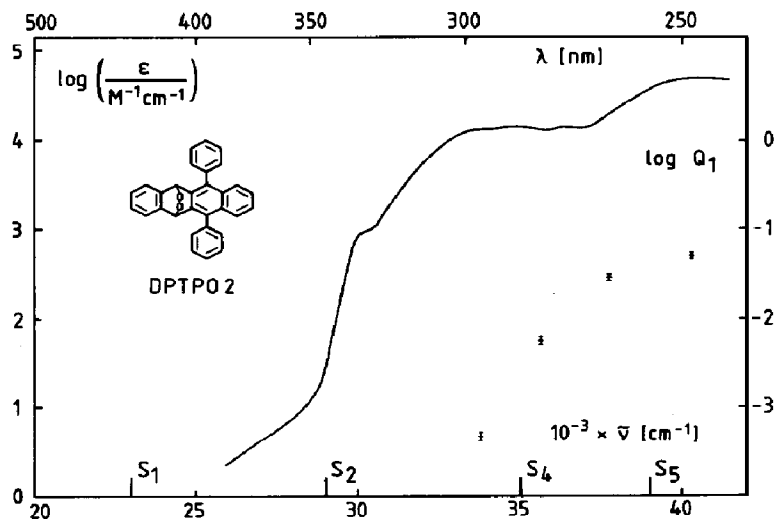


Fig. 3. Electronic spectrum of DPTP02 (solvent, CH_2Cl_2): $\bar{\epsilon}$, values for the quantum yield Q_1 with error limits; $S_1 - S_5$, energy locations of excited singlet states.

reveal an obvious relationship with regard to their band forms although their similarity is less close. In particular, the extinction coefficients ϵ of DPTP02 are about 60% larger than those of RUBPO between 33 000 and 37 000 cm^{-1} .

The similarity between the electronic spectra is caused by common structural characteristics of the molecular frames. Both carbon atoms connected by the peroxide bridge are sp^3 hybridized and interrupt the resonance interaction between the π electronic systems of the naphthalene and the benzene moieties, which arise from the tetracene system after peroxidation.

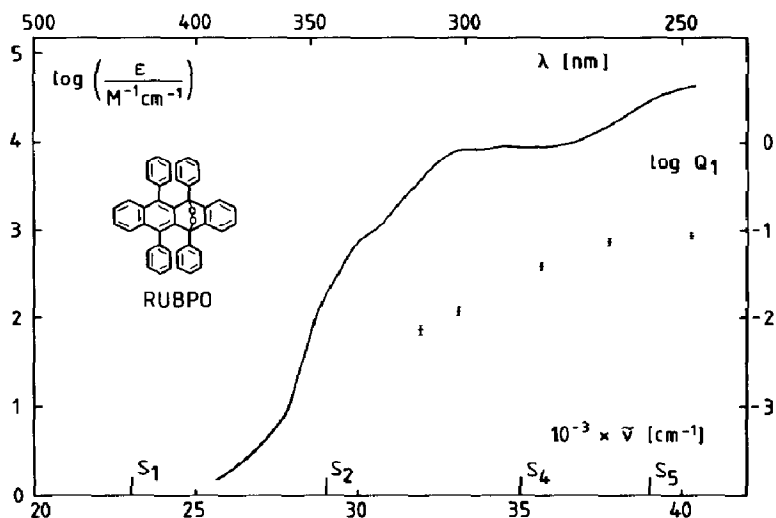


Fig. 4. Electronic spectrum of RUBPO (solvent, CH_2Cl_2): $\bar{\epsilon}$, values for the quantum yield Q_1 with error limits; $S_1 - S_5$, energy locations of excited singlet states.

Furthermore they separate these systems from the electronic system of the peroxide bridge. Therefore, to a first approximation the lowest excited state manifold of the endoperoxides can be considered to comprise the energy levels of these three chromophores.

The lowest excited singlet states of the chromophores relevant to the endoperoxides are listed in Table 1. From a comparison of these data with the electronic spectra in Figs. 1 - 4 the singlet state systems of the endoperoxides can be derived.

The spectra of TPO and DPTP01 show features characteristic of the respective absorptions of the chromophore peroxide (PO), 2,3-dimethylnaphthalene (DMN) and *o*-xylene (XYL).

In either case the absorption levels off without structure at about $25\,000\text{ cm}^{-1}$. For endoperoxides of acenes this absorption band, which has to be attributed to the $\pi^*_{00}\sigma^*_{00}$ transition of the PO chromophore, generally extends to the visible region with ϵ values of less than $1\text{ M}^{-1}\text{ cm}^{-1}$. It corresponds to the $S_0 \rightarrow S_1$ excitation of the endoperoxides, the S_1 state being located at $23\,000\text{ cm}^{-1}$ or lower [5, 16].

From the data in Table 1 the $S_0 \rightarrow S_2$ excitation of TPO and DPTP01 is expected to be the weak 1L_b transition in the DMN chromophore occurring for DMN at $31\,000\text{ cm}^{-1}$.

Examination of the spectra in Figs. 1 and 2 reveals that this excitation is indeed of 1L_b character although it is slightly red shifted to $30\,500\text{ cm}^{-1}$.

The long wavelength onset of the S_3 (1L_a) band of both endoperoxides is observed near $33\,500\text{ cm}^{-1}$. This value is in agreement with the energy determined for the 1L_a transition in DMN.

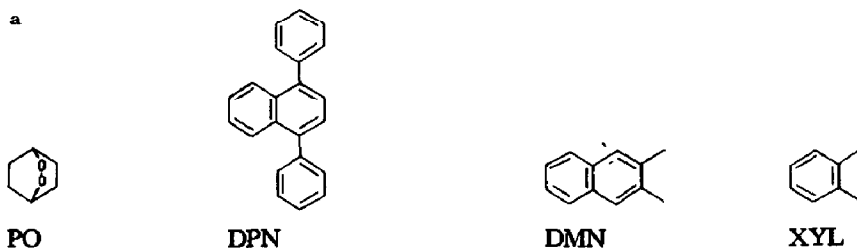
The $S_0 \rightarrow S_4$ excitation of TPO and DPTP01 should be localized in the XYL chromophore. It is expected to occur at $35\,000\text{ cm}^{-1}$, which is the

TABLE 1

Classification and energies of the lowest excited singlet states of several chromophores relevant to endoperoxides

Chromophore ^a	Classification and energies of the following singlet states					
	S ₁		S ₂		S ₃	
	Classification	Energy (cm ⁻¹)	Classification	Energy (cm ⁻¹)	Classification	Energy (cm ⁻¹)
PO	$\pi^*_{00}\sigma^*_{00}$ ^b	$\leq 23000^c$ [5, 16]				
DPN	¹ L _a	29700 ^d [17]	¹ L _b	?	¹ B _b	$\approx 39000^e$ [17]
DMN	¹ L _b	31000 ^d [17]	¹ L _a	33500 ^e [17]	¹ B _b	41500 ^e [17]
XYL	¹ L _b	35000 ^e [5]	¹ L _a	$\approx 44000^e$ [18]		

a



^bThe transition is of $\pi^*_{00}\sigma^*_{00}$ character only in the PO chromophore; in the remaining chromophores these are $\pi_{cc}\pi_{cc}^*$ transitions, classified after Platt [19].

^cEstimated on the basis of photochemical results.

^dCrossing point of fluorescence and absorption.

^eLow energy onset of the absorption band.

energy measured for anthracene endoperoxide (APO). However, this weak ¹L_b transition cannot be identified in the spectra. Because of its low oscillator strength (presumably $\epsilon \approx 400 \text{ M}^{-1} \text{ cm}^{-1}$, which is one-half the value determined for APO [5]) the $S_0 \rightarrow S_4$ transition is obscured by the strong absorption of the DMN chromophore with $\epsilon \approx 8000 \text{ M}^{-1} \text{ cm}^{-1}$.

At about $40\,000 \text{ cm}^{-1}$ a strong increase in the absorption of both endoperoxides is observed, which we ascribe to the $S_0 \rightarrow S_5$ (¹B_b) transition localized in the DMN chromophore. In DMN the strong ¹B_b transition occurs at $41\,500 \text{ cm}^{-1}$.

Summarizing the above considerations we conclude that five excited singlet states of TPO and DPTP01 can be spectroscopically identified in the investigated wavelength range to a high degree of reliability. The excitation is localized in the DMN chromophore for the S₂, S₃ and S₅ states, in the PO chromophore for the S₁ state and in the XYL chromophore for the S₄ state.

From the spectra in Figs. 3 and 4 similar definite specifications of the individual state locations are not accessible for the excited singlet states

of RUBPO and DPTP02. The reason for this is the broad and almost structureless absorptions of these endoperoxides, which of course again reflect the absorptions of the individual chromophores. 1,4-diphenylnaphthalene (DPN) also exhibits a broad and structureless absorption.

As mentioned above, the ϵ values of DPTP02 in the range from 33 000 to 37 000 cm^{-1} are about 60% larger than those of RUBPO. Presumably this may well be a steric effect since, in RUBPO, the plane of the phenyl substituents is perpendicular to the plane of the naphthalene moiety whereas in DPTP02 coplanarity is less hindered. Consequently the resonance interaction between the naphthalene system and the substituents should be strongly reduced in RUBPO.

In both endoperoxides the $S_0 \rightarrow S_1$ excitation is localized in the PO chromophore. Hence the S_1 state of both compounds has an energy of 23 000 cm^{-1} or less.

The $S_0 \rightarrow S_2$ transitions of RUBPO and DPTP01 occur at about 29 000 cm^{-1} in the DPN chromophore. The DPN chromophore may well be associated with the 1L_a transition, on account of the fact that the 1L_a excitation energy for DPN is 29 700 cm^{-1} .

The DPN chromophore also accounts for the $S_0 \rightarrow S_3$ (1L_b) and $S_0 \rightarrow S_5$ (1B_b) transitions. From the spectra, however, only the location of the S_5 (1B_b) state can be estimated. A marked absorption increase indicates that the S_5 energy is approximately near 39 000 cm^{-1} . For comparison it should be noted that the onset of the 1B_b band of the DPN chromophore occurs at 39 000 cm^{-1} . The location of the weak $S_0 \rightarrow S_3$ (1L_b) transition cannot be inferred from the spectra, as no spectral features are discernible, which would be indicative of the weak 1L_b transition in DPN.

The origin of the $S_0 \rightarrow S_4$ transition is ascribed to the XYL chromophore. Thus the S_4 (1L_b) state is expected to be at 35 000 cm^{-1} .

The singlet states of the four endoperoxides assigned in the way described are entered on the energy scale of Figs. 1 - 4.

3.2. Photochemical cycloreversion

On short wavelength irradiation (248 nm) in CH_2Cl_2 the four endoperoxides are split into the parent hydrocarbon and oxygen with quantum yields Q_1 ranging from 0.05 to 0.09. This result confirms the hypothesis that the cycloreversion is a general photochemical reaction path for endoperoxides.

A second general observation concerning the photochemistry of endoperoxides is that the quantum yields Q_1 are wavelength dependent. The values of Q_1 as functions of the irradiation wavelength are given on a logarithmic scale in Figs. 1 - 4 additionally to the spectra.

The $S_1(\pi^*_{00}\sigma^*_{00})$ state of endoperoxides is photochemically inactive with respect to cycloreversion. This is well understood in terms of state correlation diagrams [11]. The reaction channel of cycloreversion becomes accessible, however, on excitation to the $S_2(\pi_{cc}\pi^*_{cc})$ state. For most of the endoperoxides investigated so far almost constant wavelength-independent

quantum yields have been observed throughout the spectral region of the $\pi_{cc}\pi^*_{cc}$ bands, provided that the photon energy exceeds the excitation energy of the lowest $\pi_{cc}\pi^*_{cc}$ state [5, 7, 10, 15]. Apparently cycloreversion of these compounds originates from the thermalized $S_2(\pi_{cc}\pi^*_{cc})$ state. Only for TPAPO is a second increase in Q_1 with decreasing irradiation wavelength λ found, presumably in the S_2 - S_3 overlap region. Also for TPAPO the values of Q_1 subsequently reach a plateau [6], indicating an additional reaction path, which leads from a thermalized higher excited singlet state to cycloreversion.

Obviously the endoperoxides of the tetracene series deviate significantly from the general behaviour described above. Throughout the wavelength range investigated, *i.e.* in the region of the $\pi_{cc}\pi^*_{cc}$ transitions, increasing values of Q_1 are observed with decreasing λ , without approaching a definite plateau in Q_1 . Whereas DPTP01, TPO and RUBPO exhibit roughly similar marked wavelength dependences of Q_1 the relation between λ and the quantum yield is even more pronounced for DPTP02.

To be able to exclude a specific effect of the solvent CH_2Cl_2 on this unusual behaviour, $Q_1 = f(\lambda)$ has also been investigated for DPTP01 in heptane. As can be seen from Fig. 2, quantum yields about twice as large have been obtained in heptane; nevertheless the wavelength dependence is similar to that in CH_2Cl_2 . This confirms the assumption that the strong wavelength dependence of Q_1 throughout the $\pi_{cc}\pi^*_{cc}$ bands is an intrinsic property of these endoperoxides.

The constantly increasing quantum yields reveal that several upper excited states lead to cycloreversion for the endoperoxides of the tetracene series. On the basis of the experimental results, however, we cannot distinguish whether the cycloreversion channel originates from vibrationally hot or from thermally equilibrated excited electronic states. However, from a comparison with the photochemistry of the endoperoxides investigated so far (see above), we presume that cycloreversion is reached from a number of different thermalized upper excited singlet states.

This should result in a stepwise increase in Q_1 with λ , corresponding to our results for TPAPO [6], provided that the energy gaps between the respective states are sufficiently large to prevent distortions by line broadening effects caused by solvent and heat (about 2000 - 4000 cm^{-1} at room temperature). Since there are four singlet states ($S_2 - S_5$) lying energetically close to each other in the tetracene endoperoxides investigated it is most likely that the stepwise wavelength dependence of Q_1 will only be found in future low temperature studies in which more Q_1 values will have to be determined within considerably smaller wavelength intervals.

Nevertheless our present results already clearly indicate that the thermalized S_2 state of these compounds is photochemically inactive for cycloreversion. This is especially obvious for DPTP02. At 33 800 cm^{-1} , well beyond the energetic location of S_2 , the quantum yield is still considerably small ($Q_1 = 0.0005$). For DPTP01 and TPO values of $Q_1 \leq 0.007$ are measured below S_3 and for RUBPO a value of merely $Q_1 = 0.007$ is obtained at 31 900 cm^{-1} , *i.e.* much higher than the thermalized S_2 state.

From these results we conclude that for the compounds investigated the reaction path of cycloreversion is accessible with appreciable quantum yields only from higher excited singlet states S_n ($n \geq 3$).

To provide for a better understanding of the inactivity of the S_2 states for cycloreversion we now consider the respective competing processes in more detail. Q_1 is defined as the ratio of the rate constant for oxygen release to the sum of the rate constants for all the processes deactivating the reactive excited state:

$$Q_1 = \frac{k_R}{\Sigma k_D + k_R} \quad (1)$$

As, in contrast with endoperoxides of the tetracene series (e.g. TPO), excitation to the S_2 state of endoperoxides of the anthracene series (e.g. APO) leads to cycloreversion then $\Sigma k_D(\text{TPO}) \gg \Sigma k_D(\text{APO})$ and/or $k_R(\text{TPO}) \ll k_R(\text{APO})$ have to be valid.

The deactivation of the $S_2(\pi_{cc}\pi^*_{cc})$ states of TPO (the 1L_b state of the DMN chromophore) and of APO (the 1L_b state of the XYL chromophore) may proceed either by intersystem crossing (ISC) to the triplet manifold of the respective chromophores or by IC to $S_1(\pi^*_{00}\sigma^*_{00})$, i.e. by intramolecular energy transfer to the PO chromophore.

For benzene and naphthalene the energy gap between the 1L_b states and the nearest lower triplet states is only 1400 cm^{-1} . Therefore ISC may be an efficient deactivation channel for the S_2 states of APO and TPO. Actually the rate constants k_{ISC} for ISC for both compounds, which are related to XYL and DMN respectively, are rather large and amount to $1.3 \times 10^7 \text{ s}^{-1}$ for benzene and $1.5 \times 10^6 \text{ s}^{-1}$ for naphthalene [20]. Nevertheless these values are apparently too small for ISC to compete effectively with IC, because otherwise $\Sigma k_D(\text{TPO}) \ll \Sigma k_D(\text{APO})$ would be valid, in contrast with the experimental results.

Thus the deactivation of the S_2 states most probably occurs by IC to S_1 . This assumption is additionally confirmed by the observation that the irreversible rearrangement reaction of APO, which most probably proceeds from the $S_1(\pi^*_{00}\sigma^*_{00})$ state, occurs with a quantum yield $Q_{dec} = 1 - Q_1$ on irradiation of the $S_2(\pi_{cc}\pi^*_{cc})$ band [5].

With decreasing energy gap ΔE between S_2 and S_1 an increase in the $S_2 \rightarrow S_1$ IC is expected. This is valid for both IC between singlet states of one individual chromophore and IC between singlet states of different chromophores, the latter occurring by intramolecular energy transfer following the electron exchange mechanism. Since, for TPO, $\Delta E \approx 7500 \text{ cm}^{-1}$ and, for APO, $\Delta E \approx 12000 \text{ cm}^{-1}$, the relation $\Sigma k_D(\text{TPO}) \gg \Sigma k_D(\text{APO})$ is applicable to the deactivation $S_2(\pi_{cc}\pi^*_{cc}) \rightarrow S_1(\pi^*_{00}\sigma^*_{00})$.

However, k_R may also be a function of the excitation energy, as indicated by the correlation between the Q_1 values and the excitation energies. Since the S_2 state of TPO is about 4500 cm^{-1} lower in energy than the S_2 state of APO and, moreover, since for TPO the excitation energy is dispersed over a considerably larger part of the molecular frame (DMN), it

follows that

$$k_R(\text{TPO}) \ll k_R(\text{APO})$$

Thus, both premises for a satisfactory explanation of the photochemical inactivity of the S_2 states of the endoperoxides of the tetracene series are fulfilled.

Comparable conditions in respect to k_R and k_{IC} are only given for the excitation to the 1L_b state of the XYL chromophore, *i.e.* excitation to the S_2 state of APO and to the S_4 state of TPO and DPTP01. Nevertheless the Q_1 values of the endoperoxides of the tetracene series are still about one order of magnitude smaller than those of the endoperoxides of the symmetrical anthracenes with $0.22 \leq Q_1 \leq 0.35$ [4].

However, this difference is qualitatively well understood when it is taken into consideration that the extinction coefficients of the 1L_b transition in the XYL chromophore are also about one order of magnitude smaller than those of the DMN chromophore around $35\,000\text{ cm}^{-1}$.

Therefore, the DMN chromophore acts as an effective inner filter. Consequently, the probability of direct excitation of the 1L_b state of the XYL chromophore by absorption of photons with an energy of $35\,000\text{ cm}^{-1}$ is about one order of magnitude smaller for TPO and DPTP01 (S_4 state) than for APO (S_2 state).

However, if the irradiation wavelength provides the required energy, then an excitation localized in the DMN chromophore can also lead to the cycloreversion of the endoperoxides. This is indicated by a significant increase in Q_1 in the region of the S_5 band.

Acknowledgments

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